shifts mentioned depends on the presence and form of the second monosaccharide. The attachment of a carbohydrate chain by an ester bond causes an upfield shift of C_{28} (about 2.7 ppm).

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were taken on a Bruker HX-90E instrument in $CDCl_3$. The hederagenin glycosides were isolated from *Caulophyllum robustum* Maxim. [12], and they had the following physicochemical properties: hederagenin, mp 318-320°C, $[\alpha]_D^{24}$ +81°; its methyl ester, mp 235-238°C, $[\alpha]_D^{24}$ +68.9°; hederagenin 3-O-α-L-arabinopyranoside, mp 226-228°C, $[\alpha]_D^{24}$ 46.3°; hederagenin 3-O-[O-β-D-glucopyranosyl-(1→2)-α-L-arabinopyranoside], mp 248-250°C, $[\alpha]_D^{24}$ +58.12°; hederagenin 3-O-[O-α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranoside], 258-260°C, $[\alpha]_D^{24}$ +12°; hederagenin 28-O-β-D-glucopyranoside, mp 222-225°C, $[\alpha]_D^{24}$ +35°; hederagenin 28-O-[O-α-L-rhamnopyranosyl-(1→4)-O-β-D-glucopyranosyl-(1→6)-β-D-glucopyranoside], $[\alpha]_D^{24}$ −1.8°. Acetylation was carried out with acetic anhydride in pyridine.

SUMMARY

1. The assignment of the signals in the ^{13}C NMR spectra of a number of acetylated hederagenin glycosides has been made and the mutual influence of the aglycone and of the carbohydrate moiety on their chemical shifts has been determined.

2. The results indicate the possibility of interpreting the spectra of the carbohydrate moiety of acetylated glycosides in order to obtain structural information analogous to the information obtained from the spectra of unacetylated glycosides.

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NEW ALKALOIDS OF *Dipthychocarpus strictus*

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UDC 547.944/945

New alkaloids with mp 57-59°C and diptamine have been isolated from the seeds and epigeal part of *Dipthychocarpus strictus* collected in Chimkent Province (KazSSR). It has been established that the base with mp 57-59°C has the structure of N,N'-di(6-methylthiohexyl)urea, while diptamine is N-isopropyl-N'-(7-methylsulfonylheptyl)urea.

In a further study of the alkaloids of the seeds of *Dipthychocarpus strictus* [1], a liquid base with bp 193-195°C, deoxodiptocarpaine, diptocarpiline [1-3], and a new alkaloid (I) with mp 57-59°C, composition $C_{15}H_{32}N_2OS_2$, M^+ 320, have been isolated.

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedeninii, No. 3, pp. 363-365, May-June, 1980. Original article submitted February 12, 1980.

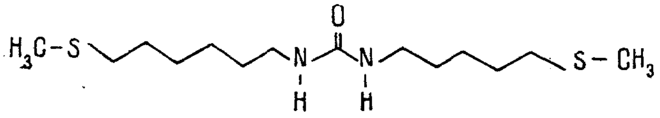
0009-3130/80/1603-0271$07.50

The IR spectrum of (I) shows absorption bands at 3335 cm^{-1} (NH) and 1630 cm^{-1} $\left(>N-C=O\right.$ The mass spectrum of the base contains the peaks of ions with m/e 320 (M^+), 305 $(M-CH_3)^+$, 273 ($M-S-CH_3$ (100%)), 227, 199, 157, 118, 75, 61, 47.

The NMR spectrum of (I) has the following proton signals, ppm: 1.10-1.90 (methylene protons), 2.04 (6 H, s, $2S-CH_3$); 2.40 (2H, t, $2S-CH_2-$); 3.09 ($2N-CH_2-$); and 5.03 (2H, 2NH groups incapable of being replaced by deuterium).

The mass spectra of (I) and of diptocarpidine [3] contain similar peaks of ions differing in m/e value by 32 mass units. The IR spectrum of (I) is characterized by the absence of the absorption bands of a S → O bond.

On the basis of the facts given above, we assumed that (I) is a deoxy product of diptocarpidine. In actual fact, when alkaloid (I) was oxidized two products were obtained the spectral characteristics of one of which proved to be identical with those of (diptocarpidine and the other with diptocarpiline [3]. Thus, it may be concluded that compound (I) has the structure of N,N'-di(6-methylthiohexyl)urea.

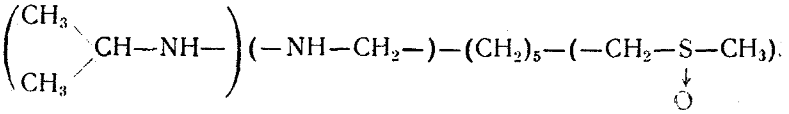


I

Continuing the separation of the combined alkaloids of the epigeal part of the plant, in addition to those found previously [3], we isolated a new base with mp 87-89°C, composition $C_{12}H_{26}N_2O_2S$, M^+ 262, which we have called diptamine (II). The IR spectrum of (II) has the absorption bands of an NH group (3350 cm^{-1}), of an amide carbonyl (1630 cm^{-1}), and of a S → O bond (1035 cm^{-1}).

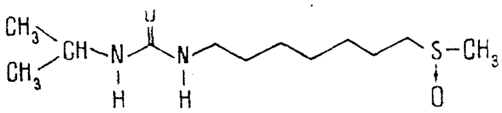
The mass spectrum of the alkaloid contained the peaks of ions with, m/e: 262 (M^+), 247 $(M - 15)^+$, 204 $(M - 58)^+$, 161, 132, 77, 69, 58, and 44. The NMR spectrum of diptamine includes signals of the following protons: $-CH\langle^{CH_3}_{CH_3}$ (1.13 m.d., 6H, d, J = 8 Hz); $-(CH_2)_5-$ (1.25-1.75 m.d., 10 H, m); $CH_3-S{\to}O$ (2.52; 3H, c); $-CH_2-S{\to}O$ (2.65, 2H, kv); $-CH_2-N\langle$ (3.07, 2H, d, J = 6 Hz); $>CH-N\langle$ (3.79, 1H, m); and two NH groups (5.07 and 5.26, 1 H, d, J = 8 Hz and 1 H, t).

Thus, diptamine has the following developed formula



$$\left(\begin{matrix}CH_3\\ \\ CH_3\end{matrix}\!>CH-NH-\right)(-NH-CH_2-)-(CH_2)_5-(-CH_2-\underset{\substack{\downarrow\\ O}}{S}-CH_3).$$

The presence in the mass spectrum of (II) of strong peaks of ions with m/e 58 and 44 (similar to the mass spectrum of isopropylurea) showed that diptamine is a N-alkyl derivative of isopropylurea. All these results agree with those for the alkaloid diptocarpamine [4]. The difference of 14 m/e in the molecular weights of diptamine and diptocarpamine shows that (II) is a homolog of diptocarpamine differing from it by one methylene group. Consequently, the structure of N-isopropyl-N'-(7-methylsulfonylheptyl)urea can be suggested for diptamine.



EXPERIMENTAL

Thin-layer chromatography was carried out in a fixed layer of silica gel of type LS 5/40 μ. The following solvent systems were used: 1) benzene–chloroform–methanol (5:3.5:1.5) and 2) chloroform–methanol (9:1). The Dragendorf reagent and iodine vapor were used for revealing the spots.

The IR spectra were obtained on a UR-20 instrument (tables with KBr) the mass spectra or a MKh-1303 mass spectrometer, and the NMR spectra of a JNM-4H-100/100 MHz instrument (δ scale in $CDCl_3$.

Isolation of the Combined Alkaloids. The comminuted seeds (10 kg) were defatted with high-boiling petroleum ether, they were then moistened with 8% ammonia solution and the alkaloids were extracted with chloroform. The concentrated chloroform extract was treated with a 5% solution of H_2SO_4, and the acid solution was made alkaline with gaseous ammonia and was re-extracted with chloroform. This gave 9.2 g of combined alkaloids.

The concentrated chloroform extract contained alkaloids which were no longer extracted by dilute acid. Therefore, the extract was evaporated to dryness and the viscous residue was dissolved in ether. When the ether solution was treated in the same way as described above, an additional 3.8 g of combined alkaloids was obtained.

Separation of the Combined Alkaloids. The mixture of bases (9.2 g) was chromatographed on a column of silica gel (1:20). Elution was carried out successively with hexane, benzene, benzene–chloroform, chloroform, and chloroform–methanol in various ratios. The benzene eluates yielded a liquid base with bp 193-195°C (1.2 g), R_f 0.85 (system 2), the benzene–chloroform eluates yielded deoxodiptocarpaine (0.2 g) and the chloroform eluates yielded a base with mp 57-59°C (0.71 g) and diptocarpiline (0.11 g).

Isolation of Diptamine. The combined alkaloids extracted from the epigeal part of the plant by chloroform [3] (34 g) were separated according to their solubilities in acetone, chloroform, and methanol. The chloroform-soluble fraction (17.2 g) was separated on a column of silica gel. Elution with benzene–chloroform (9:1 and 8:2) yielded a liquid base (1.1 g) with bp 193-195°C, and elution with benzene–chloroform (1:1) gave diptamine (0.13 g). Diptocarpiline (0.15 g) and diptocarpidine (1.21 g) were isolated from chloroform elutates.

Oxidation of (I). A solution of 0.1 g of base (I) in 5 ml of methanol was treated with 5 ml of perhydrol. The reaction mixture left overnight and then the solvent was driven off in vacuum. This gave a mixture of crystals, which was chromatographed on a column of silica gel to give diptocarpiline (0.01 g) and diptocarpidine (0.049 g).

SUMMARY

1. From the combined alkaloids of the seeds of *Dipthychocarpus strictus* collected in Chimkent province (KazSSR) has been isolated a liquid base with bp 193-195°C, deoxodiptocarpaine, diptocarpiline, and a new alkaloid with mp 57-59°C, and from the epigeal part of the plant the new alkaloid diptamine.

2. As the result of a study of spectral characteristics and also a comparison with known alkaloids, it has been established that the base with mp 57-59°C has the structure of N,N'-di(6-methylthiohexyl)urea, while diptamine is N-isopropyl-N'-(7-methylsulfinylheptyl)urea.

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